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ABSTRACT

Photoelectrocatalysis of the oxygen evolution reaction remains a primary challenge for development of tandem-absorber solar fuels generators due to the lack of a photoanode with broad solar spectrum utilization, large photovoltage, and stable operation. Bismuth vanadate with 2.4–2.5 eV band gap has shown the most promise because its photoactivity down to 0.4 V vs RHE is sufficiently low to couple to a lower-gap photocathode for fuel synthesis. Through development of photoanodes based on the FeWO_4 structure, in particular Fe-rich variants with addition of about 6% Bi, we demonstrate the same 0.4 V vs RHE turn-on voltage with a 2 eV band gap metal oxide, enabling a 2-fold increase in the device efficiency limit. Combinatorial exploration of materials composition and processing facilitated synthesis of n-type variants of this typically p-type semiconductor that exhibit much higher photoactivity than previous implementations of FeWO_4 in solar photochemistry. The photoanodes are particularly promising for solar fuels applications given their stable operation in acid and base.

TOC GRAPHICS

Photoelectrocatalysis of the oxygen evolution reaction (OER) enables harvesting of solar energy for technologies such as solar fuel generation in which water oxidation is coupled to fuel synthesis.¹ Given their unique oxidative stability, metal oxides are excellent candidate photoanodes but no material to date has met the requirements of (i) effective utilization of the solar spectrum, which requires a band gap energy no larger than about 2 eV; (ii) sufficient photovoltage to couple to a photocathode, which for fuel synthesis using a smaller-gap photocathode corresponds to a flat band potential below about 0.6 V vs RHE; and (iii) stable photoanode operation, which requires either thermodynamic stability or self-passivation. A wide variety of electrodes employing high efficiency semiconductors, such as the recent report of IrO₂-protected InGaN,² have demonstrated excellent solar utilization and photovoltage, but the liability of single-point defects in the protective layer causing semiconductor corrosion limits the viability of such photoanodes and makes self-passivation a minimum requirement for electrolyte-immersed operation. Many metal oxides meet this requirement but even the few photoactive materials suffer from large band gap energies that lead to ineffective utilization of the solar spectrum and/or insufficient photovoltages for high-efficiency tandem devices.^{1,3}

The photoanode requirements noted above are ordered by increasing ability to improve properties through optimization of morphology, doping/alloying, and protective and/or catalytic coatings. For example, alloying and morphology optimization of BiVO₄ has improved its initial reported above-gap external quantum efficiency (EQE) from about 10%⁴ to above 90%,⁵ and recent optimization of multi-layer coatings has improved stability and lowered the turn-on voltage (lowest potential where photocurrent is observed, which can be no lower than the flat band potential) from 0.4 V vs RHE to 0.2 V vs RHE.⁶ However, improving solar spectrum utilization with materials engineering has been relatively unsuccessful, highlighting the importance of

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3 discovering photoanode materials with low band gap energy that can be further developed into
4 efficient photoanodes. Fe_2O_3 and WO_3 are classic photoanode materials, making iron tungstates a
5 promising search space for new photoanodes. Previous combinatorial exploration of this space
6 identified modest improvements to photoactivity with mixtures of the binary oxides,⁷ Fe-alloyed
7 W_5O_{14} ,⁸ and Fe_2WO_6 .⁸ However, all reported photoanodes in this composition space suffer from
8 intrinsically limited photovoltage and low carrier diffusion length.⁹ To further explore iron
9 tungstates, we explore their combination with Bi and employ different processing conditions that
10 prove to be critical for the synthesis of n-type FeWO_4 , whose 1.95 ± 0.1 eV band gap, 0.4 V vs RHE
11 turn-on potential near its 0.35 ± 0.1 V vs RHE flat band potential, and self-passivation in both acid
12 and base electrolytes makes it the first metal oxide to meet the 3 primary photoanode requirements.
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17 Exploration of Bi-W-Fe oxides proceeded through synthesis of combinatorial metal oxide
18 libraries using 2 complementary methods to gauge the effects of materials processing. Both
19 libraries were prepared by sputter deposition of metal targets onto a 100 mm-diameter $\text{SnO}_2:\text{F}$
20 (FTO) coated glass substrate and subsequently annealed in air at 610 °C for 1 hour (see Table S1,
21 ESI). One library was deposited as an oxide using 10% O_2 in the sputter atmosphere, resulting in
22 relatively weak optical absorption (Table S1), whereas the film deposited as a metal using only Ar
23 as sputter gas exhibited high optical absorption over a broad composition range and became the
24 focus of photoelectrochemical (PEC) characterization. Using a previously reported scanning
25 droplet cell for high throughput screening,¹⁰ characterization of the spectral photoresponse at 1.23
26 V vs RHE was performed on 215 compositions in aqueous pH 9 borate electrolyte with 0.01 M
27 sodium sulfite as sacrificial hole acceptor (SLF9) using toggled-illumination chronoamperometry
28 (CA). While the photocurrent was measured using 4 light emitting diodes (LEDs) spanning 2.07
29 to 3.2 eV, the photocurrent at 2.4 eV (Figure 1) is particularly important since appreciable
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photoresponse at this photon energy demonstrates utilization of lower-energy photons than state-of-the-art photoanode BiVO₄. Such photocurrent was observed near the Fe-W binary line with Fe concentration between 0.5 and 0.7 and Bi concentration below 0.2, prompting the choice of Fe_{0.56}W_{0.38}Bi_{0.06}O_z (circled in Figure 1) for further characterization.[‡]

Figure 1. The photocurrent density under 2.4 eV illumination ($J_{2.4\text{eV}}$) mapped over both the library position space (a) and the composition space (b) of the Bi-W-Fe ternary oxide library in aqueous pH 9 borate electrolyte with 0.01 M sodium sulfite. The red circle refers to the Fe_{0.56}W_{0.38}Bi_{0.06}O_z

sample discussed below, and the other high photocurrent density sample ($\text{Fe}_{0.54}\text{W}_{0.35}\text{Bi}_{0.11}\text{O}_z$) is further characterized in Figure S2.

X-ray diffraction (XRD, Figure S4a) characterization of the sample revealed that FeWO_4 is the primary phase coexisting with a Bi_2O_3 minority phase. The spectral transmittance, total reflectance, and absorption coefficient are shown in Figure 2a and are assumed to be representative of the FeWO_4 structure given the small amount and high transparency of Bi_2O_3 . The sample exhibits absorption over the entire measured wavelength with absorptivity exceeding $4 \times 10^4 \text{ cm}^{-1}$ for photon energies above the $1.95 \pm 0.1 \text{ eV}$ direct-allowed band gap, determined by Tauc analysis (Figure 2b). Similar band gap energies for FeWO_4 have been reported with nanocrystal samples,¹¹ but larger band gap energies up to 2.7 eV have also been reported.¹²⁻¹⁴ The external quantum efficiency (EQE, also referred to as the incident photon to current efficiency) from the CAs at 1.23 V vs RHE is plotted in Figure 2b, revealing photoactivity with the 2.07 eV LED, just above the band gap energy, and higher EQE from 3% to 6% at higher photon energies. Direct comparison to other $\sim 2 \text{ eV}$ band gap metal oxides is enabled by our previous identification of several copper vanadate photoanodes,^{3, 15} and Figure S3 demonstrates that $\text{Fe}_{0.56}\text{W}_{0.38}\text{Bi}_{0.06}\text{O}_z$ provides a 10-fold improvement in EQE with 2.4 eV illumination. Improved EQE at this photon energy is important not only for defining a path to move beyond BiVO_4 , but also for differentiating FeWO_4 from low-gap oxides like the copper vanadates whose indirect band gap leads to low EQE at photon energies below the considerably higher direct band gap.¹⁶

Figure 2. (a) Spectra of the normalized transmittance T , normalized total reflectance R , and absorption coefficient α for $\text{Fe}_{0.56}\text{W}_{0.38}\text{Bi}_{0.06}\text{O}_z$, calculated using the thickness indicated by the inset cross-section scanning electron microscopy image. (b) Spectral EQE of this sample in sulfite-containing pH 9 electrolyte using 4 different LEDs (2.07, 2.4, 2.74, and 3.2 eV) with horizontal error bars indicating the LED line widths. The direct-allowed Tauc plot (red) indicates a $1.95 \pm 0.1 \text{ eV}$ direct band gap (intersection of black dashed lines).

With this demonstration of excellent solar spectrum utilization, we turn to characterization of the photovoltage via toggled-illumination cyclic voltammetry (CV) on the $\text{Fe}_{0.56}\text{W}_{0.38}\text{Bi}_{0.06}\text{O}_z$ sample with 2.4 eV illumination (Figure 3a), both with and without sodium sulfite. The absence of transient photocurrent density spikes under toggled illumination indicates low carrier surface

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3 recombination,¹⁷ and the substantially larger photocurrent with the hole scavenger indicates that
4 an OER co-catalyst will be required for deployment as a photoanode. To validate this result from
5 high throughput screening, conventional PEC characterization was performed with front-side AM
6 1.5G illumination in the same pH 9 electrolyte both with and without the hole scavenger using a
7 0.435 cm² epoxy-encapsulated electrode cut from the library plate. The resulting CVs of Figure
8 3b are in excellent agreement with the corresponding high throughput measurements of Figure 3a.
9 The CVs in SLF9 electrolyte provide the best quantification of the photovoltage provided by this
10 semiconductor, indicating a turn-on potential of approximately 0.4 V vs RHE, matching the value
11 for optimized, uncoated BiVO₄.⁶ Achieving the same turn-on voltage with 2 eV instead of 2.4-2.5
12 eV band gap has significant implications for tandem device efficiency. Using the Fountaine et al.¹⁸
13 model for tandem photoelectrochemical water splitting cells, this corresponds to a more than
14 doubling of the maximum device efficiency, from approximately 8% to 18% under "ideal"
15 conditions or approximately 7% to 16% under "realistic" conditions.

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17 With this demonstrated ability to enable high efficiency tandem solar fuels generators, we
18 investigate the stability criterion, starting with the calculated Materials Project Pourbaix energetics
19 of the FeWO₄ system in Figure S9.¹⁹ Like BiVO₄, FeWO₄ is only thermodynamically stable at
20 moderate pH and low potential, requiring passivation or protection layers to achieve stable
21 photoanode operation.²⁰ A desirable quality of the FeWO₄ Pourbaix diagram is the availability of
22 anodic protection layers that may provide self-passivation. At OER potentials, Fe₂O₃ is a stable
23 self-passivation layer above pH 1, and WO₃ is a stable self-passivation layer below pH 5. From
24 this analysis, the FeWO₄-based photoanode should also be operable in strong acid, which we
25 evaluated using a neighboring sample with as-synthesized composition Fe_{0.59}W_{0.35}Bi_{0.06}O_z by
26 performing a toggled illumination CV in 0.1 M H₂SO₄ with 0.1 M methanol added as a hole
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scavenger (MET1.4, Figure S1a). While the photocurrent density is lower in the pH 1.4 electrolyte, stable photocurrent during 30 min toggled-illumination at 1.23 V vs RHE indicates successful passivation in strong acid (Figure S1b).

Figure 3. (a) Front-side, toggled-illumination (2.4 eV LED) CVs of sample $\text{Fe}_{0.56}\text{W}_{0.38}\text{Bi}_{0.06}\text{O}_z$ starting with a cathodic sweep from 1.23 eV vs RHE (dashed lines) followed by the return anodic sweep (solid lines) in aqueous pH 9 borate electrolyte with (SLF9, red) and without (OER9, black) sodium sulfite. (b) CV cycles of the epoxy-encapsulated electrode (area 0.435 cm^2) containing the $\text{Fe}_{0.56}\text{W}_{0.38}\text{Bi}_{0.06}\text{O}_z$ sample in SLF9 electrolyte and subsequently in OER9 electrolyte. In each electrolyte, first 2 cycles were acquired with no illumination (“dark”, dashed lines) and subsequent 2 cycles were collected under AM 1.5G, 100 mW cm^{-2} front-side illumination with a scan rate of 0.05 V s^{-1} .

To assess longer-term stability we use SLF9, the electrolyte that provided the highest photocurrent. Using a $\text{Fe}_{0.59}\text{W}_{0.36}\text{Bi}_{0.05}\text{O}_z$ electrode, the following electrochemical procedure was repeated 34 times over the course of 7 days of testing (10 calendar days): a CV similar to that of Figure 3a was followed by approximately 50 min CA at 1.23 V vs RHE during which the sample was illuminated 97% of the time with a broadband light source (W35, Doric LEDc2, 107 mW cm^{-2} irradiance). Combined with XRF and SEM characterization, the results of Figure 4 indicate no detectable corrosion or changes in film morphology during extensive photoelectrochemical operation. The evolution of the photoactivity is somewhat surprising, with loss of approximately 20% of photocurrent through the course of the day with recovery upon exposure to air overnight. Inspection of toggled illumination CVs (Figure 4b) reveals that the degradation of photoactivity during the day is marked by a substantial change in CV shape including increased transients upon illumination toggling, which suggests a modification to the surface that introduces surface states and increases carrier recombination. Additionally considering that X-ray photoelectron spectroscopy (XPS, Figure S5, ESI) of the $\text{Fe}_{0.56}\text{W}_{0.38}\text{Bi}_{0.06}\text{O}_z$ sample PEC operation revealed a predominantly Fe^{+3} surface with Bi and W concentrations on the order of 1 at.%, and that Fe_2O_3 was identified as an impurity phase, these results are consistent with the formation of near-surface FeOOH^{21} during PEC operation that restores to Fe_2O_3 in air, with characteristic time scales that are larger than 1 hour. In this case, the FeOOH is deleterious to PEC performance and should be mitigated in future design of surface coatings.

Figure 4. Stability measurement of $\text{Fe}_{0.59}\text{W}_{0.36}\text{Bi}_{0.05}\text{O}_z$ electrode in SLF9 electrolyte over the course of 7 days with additional characterizations performed at time points indicated by the respective arrows. (a) SEM image of a nearby sample that was not electrochemically tested and thus representative of the electrode at the start of electrochemical testing. (b) 3 representative toggled-illumination CVs recorded at the beginning of day 3 (black), after 5 hours of testing on day 3 (blue), and at the beginning of day 4 (green). (c) XRF spectrum taken at the end of day 4 and comparison to the spectrum of the as-synthesized spectrum. (d) SEM image of the electrode after completion of electrochemical testing, and (e) the current density under toggled-illumination white light (97% on, 3% off) at 1.23 V vs RHE. Air exposure, in particular the 70 hours between days 4 and 5, improves initial photocurrent and slows photocurrent degradation for subsequent experiments (see SI).

The XPS-identification of an Fe-enriched surface additionally brings into question the role of surface-segregated layers during synthesis. Importantly, the FeWO_4 phase was not observed at any cation composition in the library deposited with O_2 present in the sputter atmosphere, indicating that for annealing in air, this phase is only accessible when starting with an oxygen-depleted thin

film. Indeed, inspection of the solid state thermodynamics (Figure S10) reveals that at 610 °C, FeWO_4 is the equilibrium phase for O_2 pressure below 1×10^{-4} atm, well below the $\sim 2 \times 10^{-1}$ atm of the air annealing in this work. The film deposited with oxygen is in better agreement with the equilibrium phase behavior after annealing, with XRD characterization revealing formation of Fe^{+3} containing phases such as $\text{Fe}_2\text{W}_3\text{O}_{12}$ and Fe_2WO_6 . Starting with metal thin films enables access to the FeWO_4 phase that is far from equilibrium in the air anneal, suggesting the presence of a surface layer that limits oxygen transport to the underlying film during annealing. To explore the presence of such a film, a Fe-W library (omitting Bi) was synthesized by performing the same 610 °C air anneal of a metal composition spread (see Table S1). Similar highly-absorbing material was observed for the films with thickness above approximately 500 nm, with XRD analysis revealing that FeWO_4 was only obtained as a majority phase in this thicker portion of the library, further suggesting the importance of limiting oxygen diffusion since thinner films are more amenable to equilibration with the annealing atmosphere. The highest phase concentration of FeWO_4 was observed at $\text{Fe}_{0.62}\text{W}_{0.38}\text{O}_z$, whose XRD characterization is shown in Figure S4b and reveals a presence of approximately 4% Fe_2O_3 . PEC characterization (Figure 5a) of this film demonstrated stable photoanodic performance in 4 different electrolytes: pH 1.4 and pH 6.6 containing a hole scavenger and pH 3 and pH 9 without a hole scavenger. Additional PEC characterization is provided in Figure S7 and demonstrates that while photocurrent is lower than with the Bi-containing film, the photo-response of these films is due to FeWO_4 as similar performance is obtained for its phase mixture with either Fe_2O_3 or WO_3 . Given the higher photocurrent with the Fe-W-Bi sample, the role of Bi may be related to passivation of surface defects and/or enhancement of carrier transport, motivating future investigation of the precise location of Bi in the heterogeneous film.

In total, we have observed photoactivity of electrodes with FeWO_4 majority phase and Bi_2O_3 , Fe_2O_3 , or WO_3 minority phases. The most likely common role of these 3 different minority phases is surface segregation of a high-valent oxide during synthesis that limits oxygen diffusion and enables growth of FeWO_4 , which is supported by XPS depth profiling on the as-annealed $\text{Fe}_{0.62}\text{W}_{0.38}\text{O}_z$ film (Figure S6). The near-surface layer contains primarily Fe^{+3} , and film etching leads to increased W signal and shift of Fe peaks to lower-valent values. This non-equilibrium synthesis also appears to be critical for attaining the n-type conductivity inherent to the photoanodic response of the films. Studies of single and polycrystalline samples identified FeWO_4 as a p-type semiconductor,^{22, 23} and Hoang et al.²⁴ identified the origins of the p-type conductivity through calculation of the formation energy of point defects and small polarons. As described in detail in Figure S14, at typical FeWO_4 synthesis conditions, Fe vacancies (p-type dopants) are the lowest energy point defects and hole polarons have lower formation than electron polarons. At higher Fe chemical potentials corresponding to our synthesis, oxygen vacancies (n-type dopants) are the point defects with lowest formation energy. Given the limited diffusion of oxygen into the film during annealing, oxygen vacancies are the most likely source of n-type doping, and the calculations indicate that electron polarons play an important role in n-type conductivity, especially considering their low trapping energy (0.17 eV) and migration barrier (0.12 eV), which are each lower than that of hole polarons in FeWO_4 .²⁴ While FeWO_4 has been used previously for photochemistry, the type of doping in these materials is not always clear as FeWO_4 is typically reported to inject holes via its heterojunction with an n-type semiconductor such as TiO_2 ,¹¹ ZnO ,¹² and Co_2O_3 .²⁵ Heterojunctions with Fe_3O_4 have resulted in both n-type¹³ and p-type²⁶ behavior. The only strong indications of n-type FeWO_4 in previous reports has been via nanoparticle synthesis in which the origins of n-type doping are not discussed.^{11, 12, 25}

Hoang et al.²⁴ also investigated the electronic structure of ferromagnetic (FM) FeWO₄, and we performed complementary density functional theory (DFT) calculations with antiferromagnetic (AFM) ordering to assess any difference in the electronic structure since the material is paramagnetic at room temperature.²⁷ Our DFT calculations (Figure S11) reveal highly localized Fe 3d states near and at the VBM and strong W d character near the CBM with the only substantial influence of magnetic ordering being the expected change in the spin channel of the Fe 3d states. Similar flat Fe-based valence bands are observed in both FM and AFM band diagrams, suggesting low mobility for band transport and further supporting the importance of both hole and electron polarons in charge transport. Optimization of photocurrent will require materials engineering based on further understanding of polaron conduction in FeWO₄.

Given that our photoanodes comprise the first demonstration of n-FeWO₄ thin films, we continue characterization of this doping through a series of experiments starting with Mott-Schottky analysis of a Fe_{0.62}W_{0.38}O_z film similar to that analyzed by XPS and PEC (Figures S6-S7). The Mott-Schottky plot in Figure 5b confirms the n-type conductivity of the photoelectrode. The data, as well as analogous data acquired at different frequencies (Figure S12), suggest a flat band potential of 0.35±0.1 V vs RHE, which is in excellent agreement with the turn-on voltage in Figure 3 but is not conclusive given that this film, like each of our n-FeWO₄ films, contains an impurity phase. To establish whether a more traditional synthesis of the FeWO₄ phase would yield p-type conductivity as expected, a film was deposited in 1% O₂ and annealed at 610 °C in an inert Ar atmosphere (see Table S1), yielding a phase-pure FeWO₄ whose Mott-Schottky analysis reveals p-type conductivity with flat band potential of 2.1±0.1 V vs RHE (Figure 5b). The ~1.7 V difference between the flat band potentials indicates that both n-FeWO₄ and p-FeWO₄ have their Fermi energy within 0.3 V of the respective band edge, and while FeWO₄ has a deep valence band,

the high flat band energy in the n-FeWO₄ film enables the large photovoltage observed in PEC measurements.

Figure 5. (a) 30 mins PEC stability measurements at applied potential of 1.23 V vs RHE in various aqueous electrolytes. (b) Mott-Schottky plots for two FeWO₄ electrodes with different synthesis methods acquired in SLF9 electrolyte at 2 kHz.

To provide additional characterization of the n-FeWO₄, films were prepared on insulating substrates so that electrical characterization could proceed without interference of the FTO conducting back contact. Using a Si wafer with thermal oxide coating, the Fe-W metal was deposited and annealed at 610 °C in air, resulting in the fortuitous synthesis of a phase-pure FeWO₄ film. It appeared that the Fe-rich coating observed previously formed and subsequently delaminated, perhaps during film cooling, such that the remaining film experienced similar non-

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3 equilibrium synthesis conditions described above but with no detectable Fe_2O_3 in XRD
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5 measurements due to the partial delamination. While the doping level may vary from the
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7 photoanode films due to this difference in synthesis, the measured Seebeck coefficient of $-77.1 \pm$
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9 $0.5 \mu\text{V K}^{-1}$ unambiguously demonstrates the n-type doping of the FeWO_4 in the absence of Fe_2O_3
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11 (Figure S8).
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15 The opportunities for future photoelectrode development are (i) tailored surface coatings to
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17 manage surface recombination and increase catalytic activity and (ii) optimize electrode
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19 composition and morphology to enhance polaron-based conductivity, all while maintaining n-
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21 FeWO_4 as the primary absorber material. This future work is well motivated by seminal discovery
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23 of a low-band gap, high-photovoltage, and stable metal oxide photoanode that establishes FeWO_4 -
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25 based photoanodes as the most promising route to efficient fuel generation employing solar
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27 photochemistry.
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33 ASSOCIATED CONTENT

36 **Supporting Information.**

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45 Experimental and computational details, additional photoelectrochemical and materials
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1. Lan Zhou and Aniketa Shinde contributed equally.

Notes

The authors declare no competing financial interest.

‡The oxygen stoichiometry was not measured. XRD and XPS characterization of average cation valences indicate that z is approximately 2 for all compositions discussed in the manuscript.

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